HOST-GUEST COMPLEXES OF AZAAROMATIC QUATERNARY SALTS

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Abstract-Inclusion complexes, where azaaromatic quaternary salts serve as a guest or as a host are described, along with related rotaxanes and catenanes.

I. INTRODUCTION

Recently a rapid development of the supramolecular chemistry[1,2] is observed. These problems are the subject of a lot of investigations, often of an interdisciplinary character. In this area an interesting group are host-guest complexes.[3-10] There exist various types of host-guest complexes - those where host units are crown ethers,[11-12] cyclodextrins,[13,14] cyclophanes,[15,16] azaaromatics[17-21] and their metal complexes[22] or polyazamacrocycles.[23]

In the study of synthetic approaches to host-guest systems a special attention is paid to the synthesis of tailor made systems. Molecules which can interact with other species in a well defined manner are investigated; numerous rigid systems are used for preorganizing binding groups. Various molecular architectures are examined in order to adjust the shape and size of hosts to guests.

A very important aspect of host-guest chemistry is the relationship with biological reactions.

Biological systems of Nature are complex, therefore it is necessary to construct simpler models in order to evaluate theories of photosynthesis for example. A better understanding of physico-chemical mechanisms by which photosynthetic organisms capture and store the solar energy is of a great value.

Host-guest complexes may be of use as artificial enzymes and receptors. Biological and biomimetic aspects of the study of host - guest complexes will help in their application in medicine and pharmacy; they may be also used in the sensor technique as molecular switches, or in catalysts working as enzyme analogues; they may be applied as electrodes and membranes in biology and in analytical chemistry. Among numerous types of host-guest complexes, the group of such species where azaaromatic quaternary salts play the role of a guest or of a host deserves a special attention in view of interesting properties of azaaromatic quaternary salts. In azaaromatics the nitrogen atoms are quite responsible for the formation of a great many of metal complexes[24-26] as well as for their quaternization;[27-31] the topic of numerous papers are CT complexes of azaaromatics[32-34] or of their quaternary salts.[35,36] Azaaromatic quaternary salts are important for their biological activities[29,37-39] and applications.[28,40,41]

One should emphasize here the redox reactions of quaternary azaaromatics, especially those of viologens; these compounds are electron mediators, and can be applied as electrochromic and photochromic materials, also their use in semiconductor laser technology, in electronic devices, in sensors, electrodes and membranes is possible. Interesting properties possess systems incorporating a quaternary salt moiety, for example viologen linked porphyrins, a special group of compounds described in many recent publications. Viologen mediated reactions are known, viologens are also useful in solar energy conversion and storage.

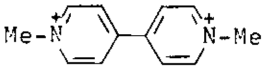
Biological activity of quaternary salts should also be mentioned here, especially their ability to intercalate into nucleic acids.

The present paper deals with host-guest complexes of azaaromatic quaternary salts,having in view on the one hand the interesting properties of quaternary salts of azaaromatics, and on the other hand the host-guest chemistry now so intensively studied; therefore it seems of interest to review species where quaternary azaaromatics play the role of a guest or of a host.

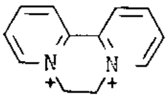
II. INCLUSION COMPLEXES WHERE QUATERNARY AZAAROMATICS ARE GUEST MOLECULES

An example of systems where the quaternary azaaromatic serves as a guest are complexes of 2,2'- and 4,4'-bipyridinium ions with biphenylene [30-34] crown ethers playing the role of host molecules.[2,42,43]

It was found that bis-orthophenylene [30] crown-10(1)forms complexes with diquat, and not with paraquat (i.e. methylviologen, MV^{2+}); due to this observation an ion-selective electrode for diquat was built.[44]

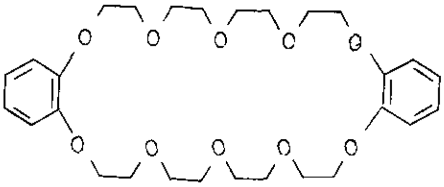


paraquat

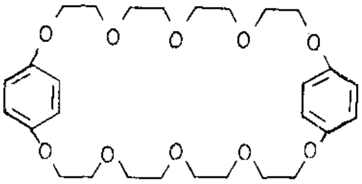


diquat

In the electrode the sensor consists of a mixture of diquat - bis-(tetraphenylborate) with 1, embedded in a PVC matrix - membrane, using 2-nitrophenyl(phenyl) ether as plasticizer. On the other hand bis-paraphenylene [34] crown-10 (2) is the host for diquat as for paraquat.[42,45-51]

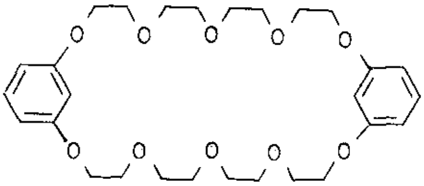


1



2

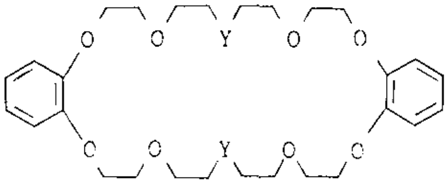
Complexes of paraquat and diquat $[PF_6]^{2-}$ salts with bis-metaphenylene [32] crown-10(3)used as a host are also known.[52]



3

Diazaanalogues of 1 may be used as hosts, too, for instance diquat (as-bishexafluorophosphate) forms strong 1:1 molecular inclusion complex with receptors 4c-f and 5a,b.[53] In such type of complexation, along with CT interactions, also hydrogen bonding, Coulombic attractions and dispersion forces are involved.

On the other hand, no complexation was observed in the case of 4a,b, probably due to the combined electronic and steric factors associated with their amide nitrogen atoms.[53]



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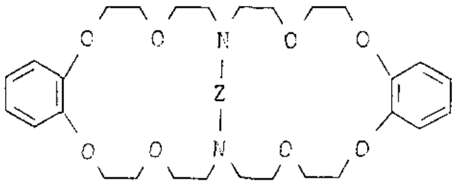
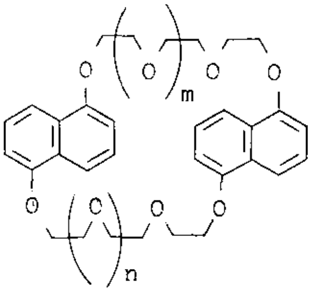


5

	Y		Y		Z
a	NTs	d	NCH_2COOEt	a	CH_2-4-$C_6H_4CH_2$
b	NCOOEt	e	NCH_2Ph	b	CH_2-4-C_6H_4O O O O O OC_6H_4-4-CH_2
c	NMe	f	NCH_2-4-C_6H_4OMe		

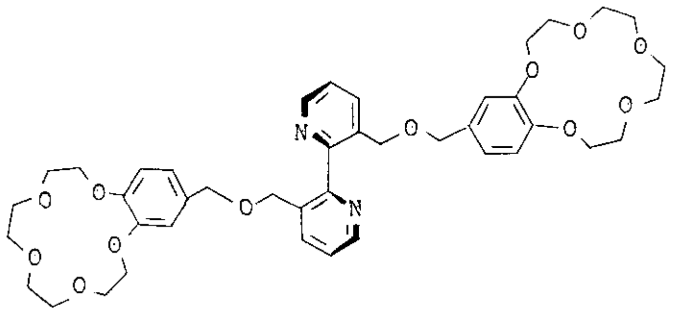
The 1:1 complex of viologen and 6 serving as a host exists in solution. However in a solid state a stacked donor-acceptor structure was found.[42,54,55]



n = 1,2,3
m = 2,3

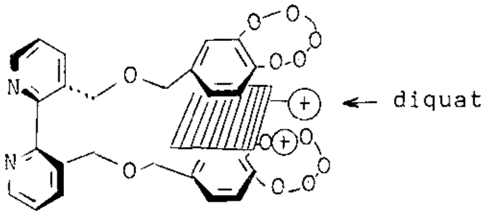
6

When acetonitrile solutions of diquat and 2,2'-bipyridyl bis crown ether(7) are mixed, the orange color occurs immediately. This is due to the CT interaction of the electron deficient diquat dication and the electron rich catechol units; an orange - red solid diquat·(7)(1:1) was isolated.



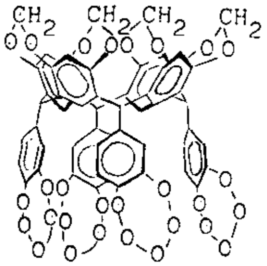
7

The results of nuclear Overhauser effect (NOE) difference spectroscopy show that it has in solution the structure (8), i.e. that the planar dicationic guest diquat intercalates between the two benzo-crown ether subunits of the host resulting in parallel stacking of aromatic rings.[56]



8

A next example is the binding of paraquat and diquat as guests of cavitands (9), (10), and (11); these host molecules have the upper bowl-like cavity and a lower benzo crown ether box-like hollow.



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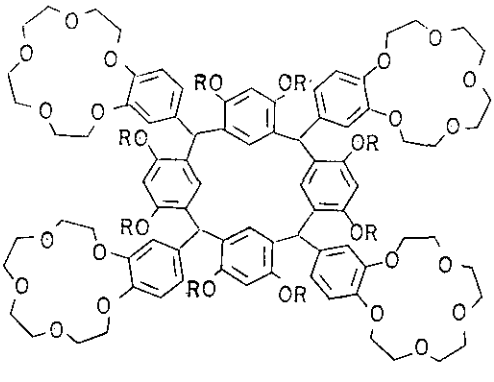
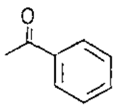


R

10



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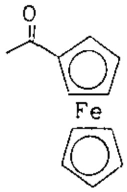
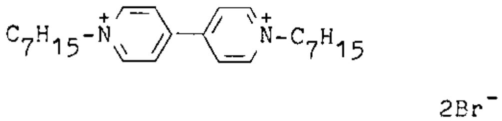


It was established by high field ^1H nmr spectroscopy that paraquat and diquat are included only into the lower cavity.[57]

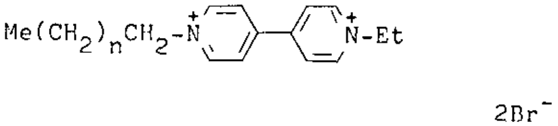
A special group of inclusion complexes are those where cyclodextrins play the role of host molecules,[14,58,59] among them there are systems with viologens as guests.[60-62]

In the complex of heptylviologen (12) and α-cyclodextrin the bipyridinium moiety of 12 is localized out of the cavity of cyclodextrin, while the heptyl chain is situated inside.[63-65]



12

Also complexes of 13 with α- and β-cyclodextrins are known.[66,67]

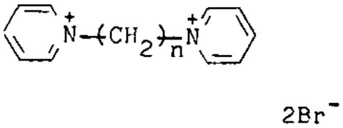


13

n = 14,16

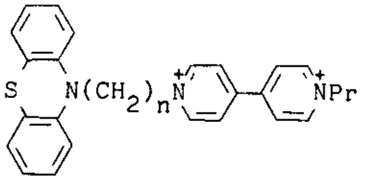
In the study of cyclodextrin complexes,[68-70] a rotaxane-type, through-ring complex of α-cyclodextrin with polymethylene bis(1-pyridinium) (14) serving as a guest was investigated.[13,71,72] Such complexes have the lifetime long enough to be separately detected in nmr time scale at 5°C. Signals of the originally equivalent pair of protons in the pyridinium and polymethylene groups are split into a pair of distinct signals on complexation.

By the use of ^1H nmr spectroscopy it was established that the stability of the formed complex increases considerably with the spacer length due to its hydrophobic interaction. The complex-induced chemical shifts suggest evolution of electromagnetic gradient along the polymethylene chain. The amount of the chemical shift change for a given pair of protons, induced by complexation, decreases rapidly with the length of the spacer chain.[13] Photoinduced electron transfer reactions of phenothiazine linked viologens 15 with α- and β-cyclodextrins were also studied.[69]



14

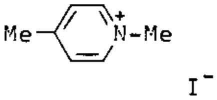
n = 6,8,9,10 and 12



15

n = 4,12

Examples of inclusion systems where cyclophanes play the role of host molecules[16,73,74] are complexes of 16–18 serving as guests, and of negatively charged cyclophanes (19a,b); these complexes are formed in alkaline water.[15]



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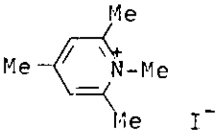

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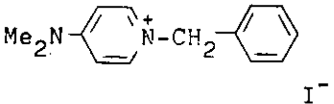

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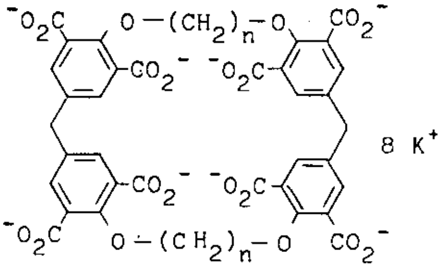
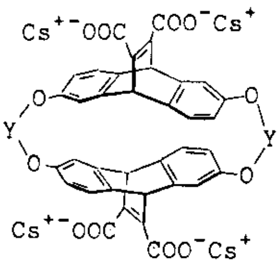


19

Describing complexes with macrocyclic cyclophanes as host molecules, there ought to be mentioned the observation that quaternization of quinoline with methyl iodide is accelerated by the presence of cyclophane (20a).[75-78] The occuring complexation is due in part to the attractive cation-π interaction between the positive charge of a guest and the polarizable electron-rich π-systems of the host.[79,80] It is suggested that the cation-π interaction is predominatly responsible for the catalysis.



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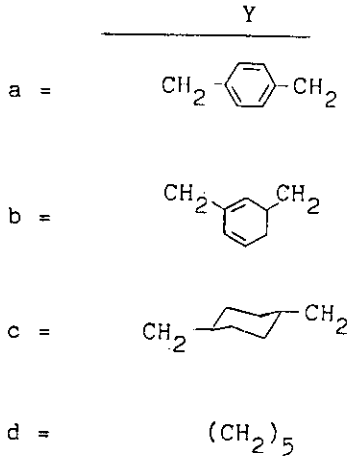
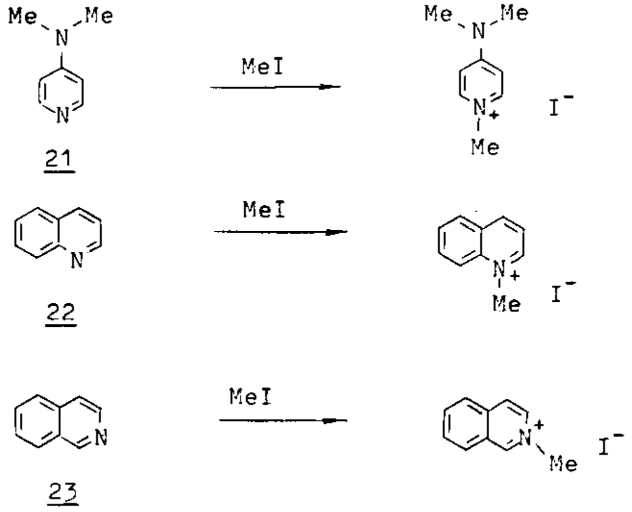


Hosts of the type (20a) may act as biomimetic catalysts in aqueous media of S_N2 reactions when their transition states bear a positive charge.[81-83] One can suppose that biological methylation reactions proceed via transition states, which are bound by cation-π interactions.

The quaternization reactions of 21, 22 and 23 with methyl iodide performed in D_2O/borate buffer proceed slowly, however when 20a is added, a considerable acceleration occurs.

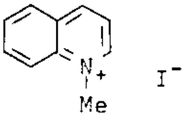


The catalysis is presumably due to the cation-π interaction; a support can be the fact that the host (20c) showing a weaker cation-π effect than 20a is also a weaker catalyst.

One ought to point out that the transition state, with only a partial positive charge is stronger bound than the product, bearing a full positive charge. This can be explained by the higher polarizability of transition states because of their long, weak bonds as compared with ground states.

It is known that enzymes preferentially bind transition states.[84] This probably may find explication in the fact that cation-π interactions are predominantly responsible for the transition-state binding. This is confirmed by the observation that the big amount of biological methylation processes is mediated by SAM and the transition states of these reactions are similar to those bound by 20a (SAM = S-adenosylmethionine).[85]

For host-guest systems where hosts are macrocyclic cyclophanes (20a-d) and guests are 24, 25 and 26, the variable temperature binding investigations in both aqueous and organic ($CDCl_3$) media were made.[86] Significant heat capacity effects were revealed; the origin of the binding force at lower temperatures is entropic and at higher temperatures enthalpic.[76-78,87-90]



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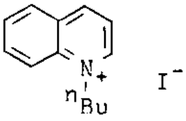

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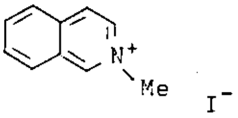


26

III INCLUSION COMPLEXES WHERE QUATERNARY AZAAROMATICS ARE HOST MOLECULES

In host-guest systems, quaternary azaaromatics can also play the role of host molecules, as an example can serve the complex of the electron deficient, rigid receptor cyclobis(paraquat-p-phenylene)tetracation (27) which incorporates isomeric dimethoxybenzenes.[49-51,91-96] Due to the ability of weak complexation in solution, 27 probably may be used in catalysis.[50]

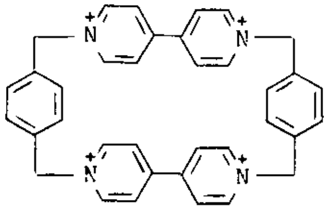
Also solid state 1:1 complexes of $27\cdot 4PF_6\cdot 2MeCN$ with hydroquinone dimethyl ether and catechol dimethyl ether are known. It is interesting that both of these complexes are intensively red, due to the retention, in the solid state, of the CT interaction observed in solution.[50,51,96]

The complexation with hydroquinone dimethyl ether does not change the overall dimensions of the macrocyclic ring (27). The predicted geometry of this complex was found by molecular mechanics geometry calculations using the AMBER force field[96] and atomic charges obtained within the AM1 SCF-MO procedure and was found to be almost identical with that observed in the X-ray crystal structure.

$27\cdot 4PF_6\cdot 2MeCN$, an inexpensive synthetic receptor is versatile in its guest acceptance, by contrast with other cyclophane hosts. It is able to form a channel structure in the crystalline state in which the rigid tetracations form an alternating charged stack bound together electrostatically with four PF_6^- counterions and also two neutral MeCN molecules.

This type of crystal packing is characteristic for the inclusion complexes formed by cyclodextrins, where intermolecular hydrogen bonding stabilizes stacks of these rigid naturally occuring receptor molecules. Like the cyclodextrins, $27\cdot 4PF_6\cdot 2MeCN$ can form inclusion complexes with a variety of substrates, some of which, e.g. hydroquinone dimethyl ether can diffuse out of and into the polar molecular chimneys of the receptor, giving the anticipated color changes.

Another macrocyclic host is 28, able to form complexes with arenes.[97]



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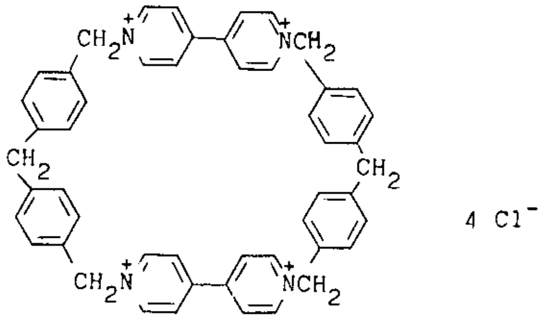
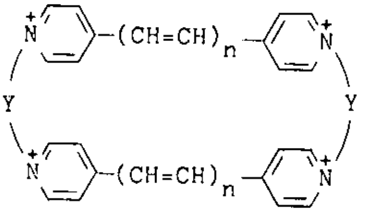
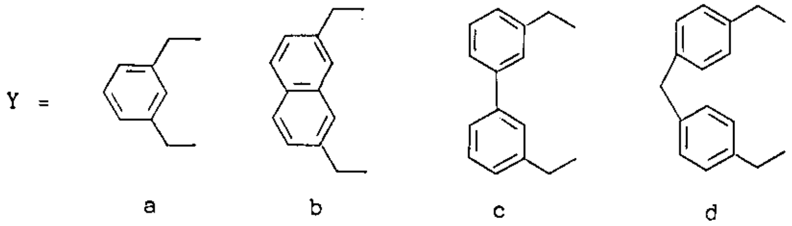


28

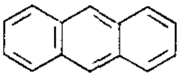
As host molecules serve also 29 and 30. In these compounds two 4,4'-bipyridinium and 1,2-bis(4-pyridinium)ethene moieties, respectively, are so parallelly arranged that they can form with guest molecules sandwich - like systems.[97]

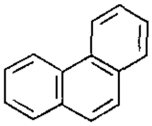


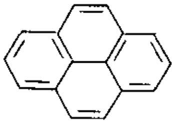
	n
29	0
30	1

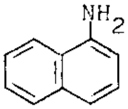


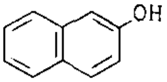
As guests can serve following compounds:

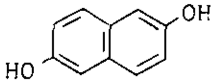


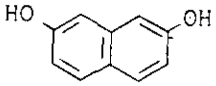








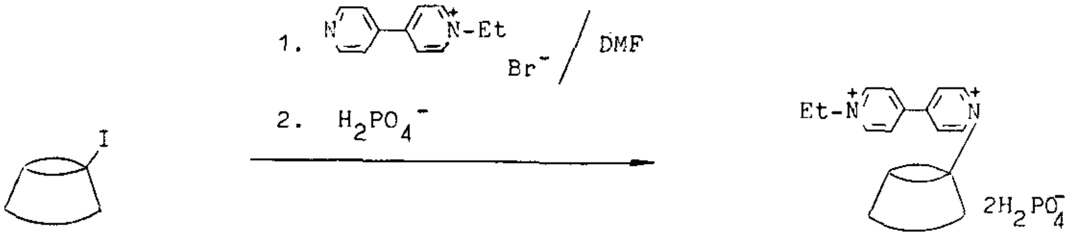




It was observed that the cyclic tetracation (30a) with a small cavity has a diminished acceptor strength, 30b and 30c have the most favorable dimensions for the majority of guests, while 30d is too wide for them. Increase of the cavity by the diphenylmethane bridges in 30d destabilizes host guest complexes; this effect should be of importance for the synthesis of intercalating compounds for nucleic acids.[98,99]

The binding strength of complexes investigated increases in the series anthracene, phenanthrene and pyrene, while a considerable decrease is observed in the case of perylene obviously being too large for all cavities.[97,100]

Studying inclusion systems useful as self-assembly-type molecular devices,[101] the synthesis of a viologen appended β-cyclodextrin (31) was performed as shown below.[102]



31

31 has the character of a host molecule and of an electron acceptor. It binds negatively charged guests, as *p*-nitrophenol anion, as well as non-charged guests like p-nitroaniline. The conformation and the binding properties of related systems were investigated by induced circular dichroism and other spectroscopic methods.[103,104]

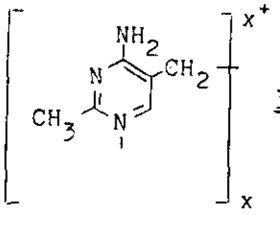
In the study of photosensitized reduction of viologens as model systems for solar energy conversion,[105] in order to retard the back reaction between the reduced species of acceptor and the sensitizer, organized assemblies such as micelles and liposomes are often applied.[106,107]

These reductions can be modified by the presence of guests because in such systems the position of the viologen moiety can be changed by the guest binding; this can be shown by induced circular dichroism results.

Photosensitized reduction of viologen-appended β-cyclodextrin (31), in aqueous solution, using Rose Bengal RB^{2-} as the sensitizer and EDTA as the electron donor was investigated in the presence of 1-adamantanol, adamantanecarboxylic acid or sodium cholate, acting as guests of 31.

It is suggested that the back electron transfer is suppressed in the presence of adamantanecarboxylic acid as a guest, and in this case the high yield of the reduction is achieved.[108]

Polycationic pyrimidinium oligomers of the type (32ab) serve as receptors for anions.[109]



32

	x
a	4
b	6

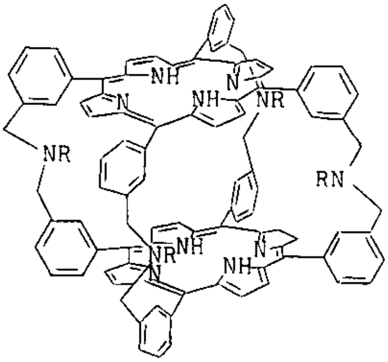
For example, [16-pyrimidinium crown-4]$^{4+}$ (32a) gives inclusion complexes with chloride and nitrate ions in methanol.[110] The chloride salt of 32a was prepared in the reaction of thiamin chloride hydrochloride with

$Ni(OAc)_2 \cdot 4H_2O$ or $Zn(OAc)_2$, while the nitrate was formed by heating thiamin nitrate in $MeOH/H_2O$ medium.

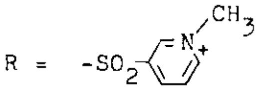
The cationic tetramer(32a) itself is cyclic, its four pyrimidine units are joined by methylene groups linking C5 and N1 atoms. However, when Cl^- or NO_3^- anions are included, 32a adopts a boat form.

It has to be pointed out that the anion coordination chemistry, especially of biologically important anions such as HCO_3^- or HPO_4^{2-} is of interest having in view biological aspects.[50,51,82,97]

As host can serve also porphyrin dimer (33) bearing N-methylpyridinium groups.[111]



33

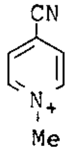


Inclusion complexes where quaternary azaaromatics are incorporated into zeolites, serving as hosts are also known.[112,113]

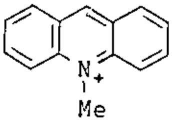
In the study of intercalation of molecular guests within intravoid space of zeolites, it was established that zeolites doped with quaternary azaaromatic acceptors can serve as sensitive color probes for the intracavity assembly of specific ion pairs and ion triplets.[114] For example the ion exchange of MV^{2+} into sodium zeolite Y can be regulated to produce zeolites containing one and two MV^{2+} species in each average supercage, MV(1.0)Y and MV(2.0)Y.

The efficient intercalation of iodide from acetonitrile solution gives colored zeolites; their diffuse reflectance spectra show the presence of CT bands of the ion pair MV^{2+} (I^-) and of the ion triplet MV^{2+} $(I^-)_2$; the separation of these two species is possible. Shape selectivity in this stepwise assemblage of ions within the supercage is controlled by the size of iodide salt M^+ I^- (M^+= Na^+, K^+, Me_4N^+, Et_4N^+, $^nBu_4N^+$).

In zeolites, the very small cations are localized within the sodalite cages (β-cages), larger are in interior cavities (α-cages, supercages), and the largest ones are in the exterior surface of zeolite crystals.[113,115-117] In order to develop a method for zeolite shape selectivity, monocationic acceptors (34) and (35) and dicationic acceptors - paraquat and diquat were exchanged into the supercage of zeolite Y.



34



35

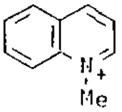
These species are convenient for this purpose, since they form highly colored crystalline salts with iodide, resulting from CT electronic transitions from the iodide donor to the organic acceptor.

Compounds (34, 35) paraquat and diquat were introduced into zeolite Y by ion exchange from aqueous solution. In this way the colorless doped zeolites were obtained. Upon mixing such doped zeolite Y with acetonitrile solution of iodide salts (Na^+, K^+, Me_4N^+, Et_4N^+) the bright coloration of the zeolite occured, while the supernatant solution remained colorless. The spectroscopic characterization of colored zeolites was performed by comparison of their diffuse reflectance spectra with those of the corresponding crystalline CT salts with iodide.[118,119]

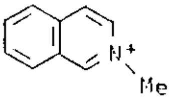
It is suggested that iodides penetrate into the zeolite supercage via ion-pair intercalation, the confirmation is the strong dependence of this process on the size of the counterion.[120]

The above experiments involving the use of organic cations as electron acceptors are a convenient probe to visually examine zeolite shape selectivity.

Zeolites doped with quaternary azaaromatic salts of different size and charge, 35-37 as well as paraquat and diquat may accept arenes.[115,121-123]



36



37

It was found that among above acceptors the most convenient is paraquat, due to its shape and charge.[121,124,125] As donors were used benzene, naphthalene, anthracene and tetracene along with their substituted derivatives.

When the solution of a donor in n-hexane, dichloromethane, acetonitrile or benzene was mixed with the methylviologen-doped zeolite Y(MV(Y);colorless), a bright coloration of zeolite took place. The diffuse reflectance spectra of colored zeolites show characteristic CT bands, the same that are obtained in solution with MV^{2+} and the arene.

In the experiments the visual examination of intermolecular complexes within the supercage of doped zeolites by the shape-selective intercalation of aromatic donors from organic solutions was made. The size and shape of arenes strongly influences the complex formation, for example 2,6-dimethoxynaphthalene gives coloration, while its 1,4-isomer does not. Each zeolite Y supercage could be occupied by two MV^{2+} dications; however under the same conditions zeolites X and A incorporated smaller amounts of MV^{2+}

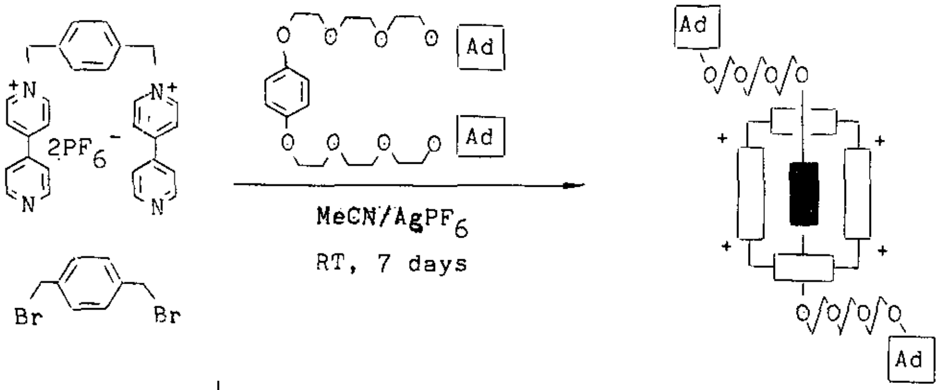
It was observed that the number of intercalated donor molecules decreases with the higher methyl substitution; for example, going from toluene to pentamethylbenzene the coloration occurs, which is not the case for hexamethylbenzene.

The efficiency of donor intercalation is strongly influenced by the solvent structure; alkanes are more effective than the chlorinated solvents. Among chlorinated solvents, their efficacy increases with chlorosubstitution in the order CH_2Cl_2 < $CHCl_3$ << CCl_4.[119,126,127]

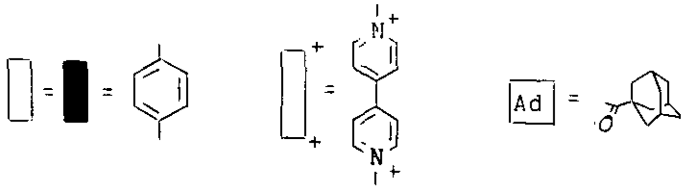
IV ROTAXANES AND CATENANES WHERE ONE UNIT IS A QUATERNARY AZAAROMATIC

In order to construct molecular electronic devices the knowledge how to self-assemble and self-replicate at the molecular level is necessary. In the study of organized molecular assemblies, [1,128-139] rotaxanes and catenanes, where one unit is the azaaromatic quternary salt were synthesised.[94,140,141] Forerunners for making such systems are host-guest molecules.

An example of a [2] rotaxane is 38 obtained in the following reaction.[140]

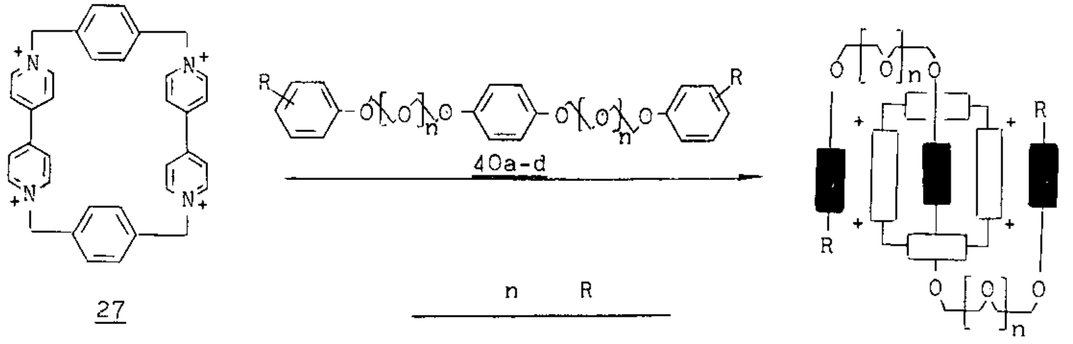


38



Rotaxanes may be compared to a bead, here cyclobis(paraquat-p-phenylene)-tetracation 27, strung onto a thread, i.e. the polyether chain. To prevent the bead from slipping off, at the ends of the thread bulky "stoppers", often triisopropylsilyl groups, or as in the case of 38, adamantyl groups are localized.

Other examples of rotaxanes are 39 obtained in the reaction of 27 with 40a-d.[142]

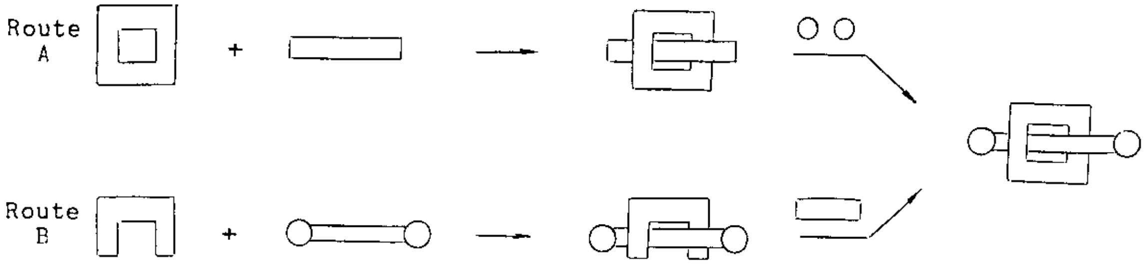


27

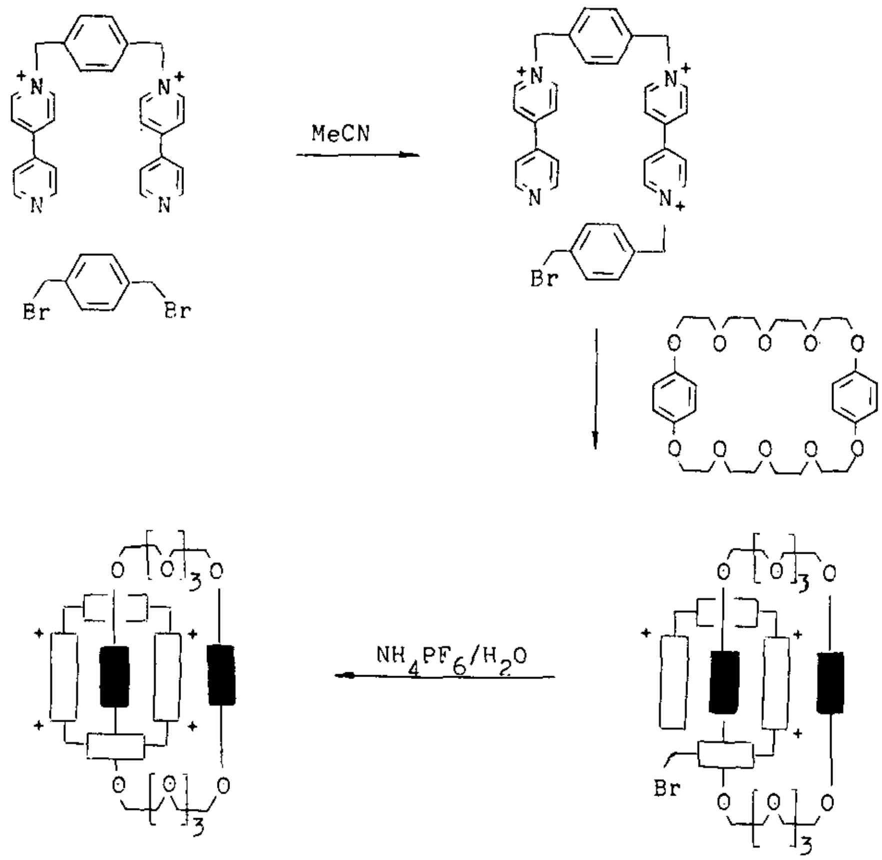
39

		n	R
40	a	2	4-OH
	b	2	$3,5-(MeO)_2$
	c	2	$4-PhCH_2O$
	d	3	$4-PhCH_2O$

There exist two routes of the synthesis of rotaxanes, schematically depicted below. One can string a complete bead onto the thread and then stopper its ends by bulky groups (route A, i.e. threading procedure) or clip the bead around the thread, already stoppered by bulky terminal groups (route B, i.e. clipping procedure)[142,143]



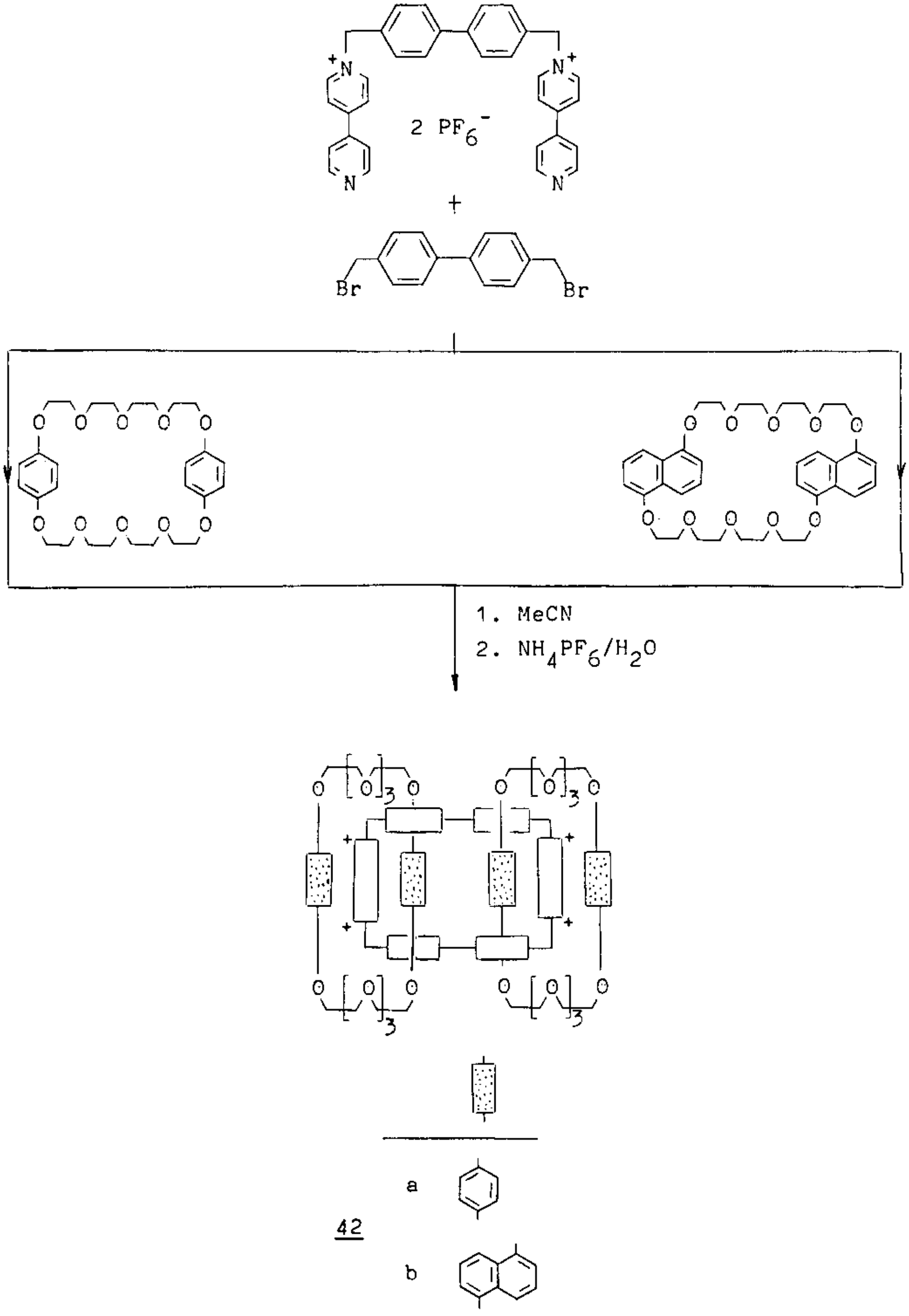
An example of [2] catenane is 41 obtained in the following way.[42,45,49-51,144-151]



41

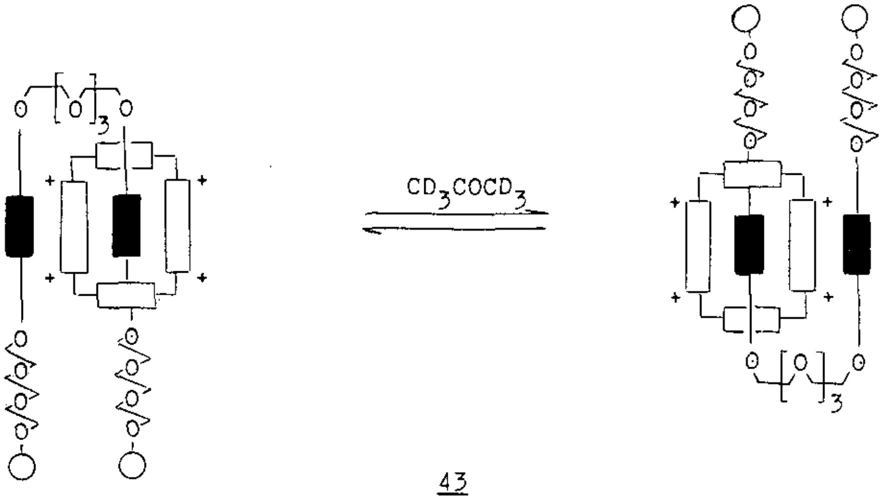
It was shown recently that 41 may also be formed from five molecules - two of bipyridine, two of p-bis(bromomethyl) benzene and one of bisparaphenylene [34] crown-10 (2) when they are subjected to ultrahigh pressure at room temperature in DMF.[149]

[3] Catenanes, for example 42a,b are also known; their synthesis proceeds as follows.[141]



42

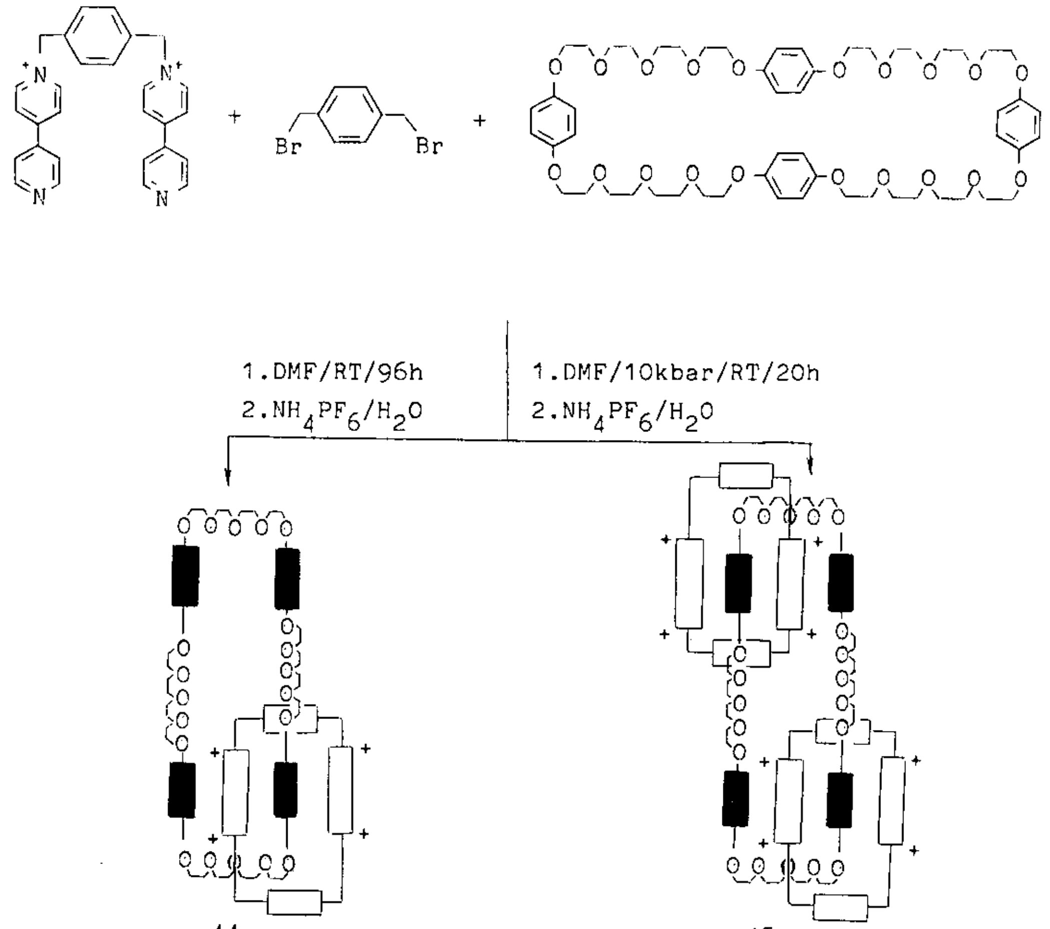
Rotaxanes and catenanes may behave like molecular shuttles or trains.[94] In the system (<u>43</u>) the tetracationic "bead" <u>27</u> moves at room temperature to and fro like a shuttle or a train ca 500 times a second between two stations A and B, as it was established with the use of dynamic ^{1}H nmr.[94,143]



<u>43</u>

○ = Si $^{i}Pr_3$

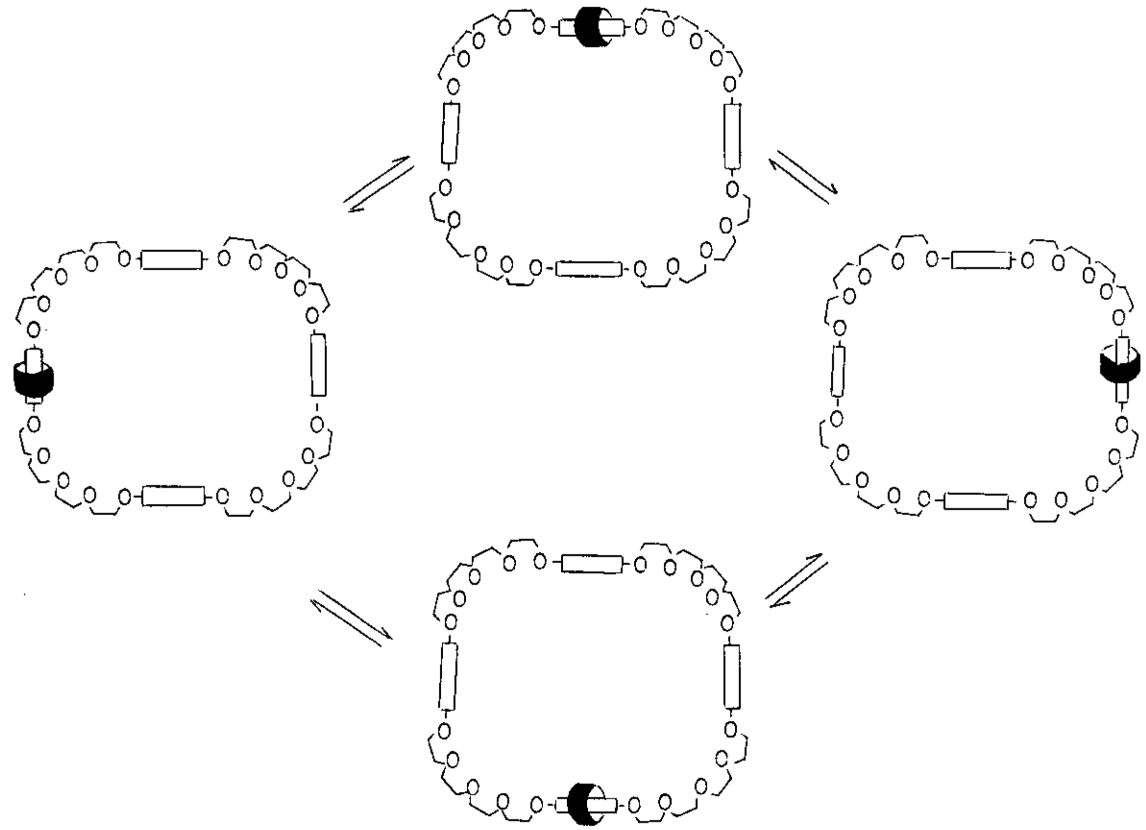
Examples of molecular trains making round-courses are [2] catenane (<u>44</u>) and [3] catenane (<u>45</u>), obtained as shown below; in the case of <u>45</u> the ultrahigh pressure is necessary.[152,153]



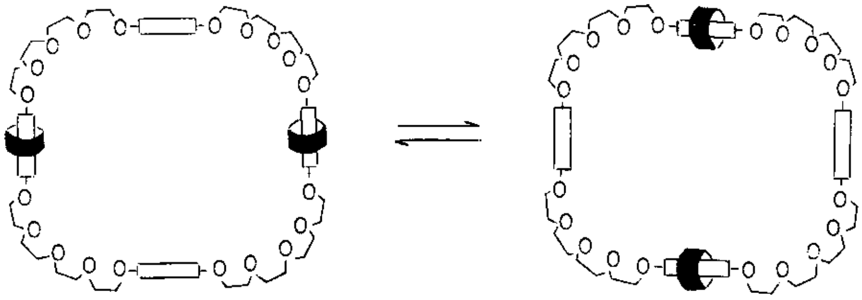
44

45

By use of dynamic ^{1}H nmr spectroscopy it was found that in 44 the train, i.e. 27 is moving 300 times a second from one station to another at room temperature:[94,153]



In the case of 45 two trains 27 moving around the circle manage to keep a free station between them and the travelling time between stations is nearly the same.[153]



Such highly ordered supramolecular structures are very promising, since self-assemblies of this kind have perspectives in construction of molecular electronic devices.[94]

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